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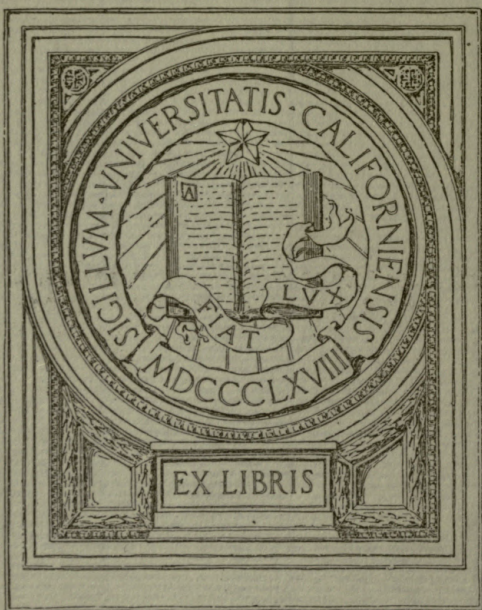
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# Intermolecular Rearrangement and Equilibrium of the Normal and Iso Propyl Bromides and Their Formation from Hydrogen Bromide and Propylene

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A DISSERTATION

PRESENTED TO THE FACULTY OF BRYN MAWR COLLEGE  
IN PARTIAL FULFILMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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BY

HELEN GOLDSTEIN RAFSKY

1922

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EASTON, PA.:

ESCHENBACH PRINTING COMPANY

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## CONTENTS

Introduction .....	5
I Rearrangement of the propyl bromides, and equilibrium in the gaseous state .....	7
Methods employed in testing the mixed bromides.....	9
II The union of hydrogen bromide with propylene.....	13
Reaction in the gaseous state	
(a) Equimolecular quantities of propylene and hydrogen bromide in large bulbs.....	14
(b) In tubes at atmospheric pressure under varying conditions.	19
Reaction of propylene and aqueous hydrogen bromide	
(a) Gaseous propylene at atmospheric pressure.....	20
(b) Liquid propylene in sealed tubes.....	21
III Dissociation of the propyl bromides.....	23
Preparation of materials.....	25
Summary.....	26





## Intermolecular Rearrangement and Equilibrium of the Normal and Iso Propyl Bromides and Their Formation From Hydrogen Bromide and Propylene

From time to time theories have been proposed with the hope that they might throw some light upon the relation which must exist between the chemical constitution of organic compounds and their physical and chemical properties. This relation is an extremely complex one, as we should expect if we accept Van't Hoff's view that each atom in a molecule exerts an influence upon every other atom in the molecule, both through space and indirectly through the intervening atoms.

This problem has remained unsolved up to the present. It is possible that some headway might be gained by a thermodynamic investigation of the behavior of some simple organic compounds. In the following investigation the relative stabilities of the monobrom propanes are studied and it is now possible for the first time, to state definitely which is the more stable. It is of great importance to find the relation between this difference in stability and the arrangement of the atoms in the two isomers.

The only similar case which has been investigated is that of the equilibrium between the monobrom derivatives of isobutane.<sup>1</sup>

Michael<sup>2</sup> believed that that compound would be most stable, in which the bromine atom was bound to the carbon atom which was most strongly under the influence of hydrogen atoms. Michael's scale of influence<sup>3</sup> is an attempt to show how this influence varies with the relative positions of the atoms. If

<sup>1</sup> Brunel, *Ber.*, **44**, 1000 (1911); *Ann.*, **384**, 245 (1911); *J. Amer. Chem. Soc.*, **39**, 1978 (1917).

Michael and Leupold, *Ann.*, **379**, 302 (1911).

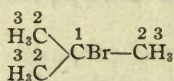
Michael and Zeidler, *ibid.*, **393**, 92 (1912).

<sup>2</sup> *J. für. prakt. Chem.*, **60**, 286, 409 (1899).

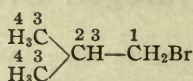
<sup>3</sup> *Ber.*, **39**, 2139 (1906).

any given atom is numbered 1, and the rest of the atoms are numbered consecutively to show their degree of removal from atom 1; then the combined direct and indirect influence upon atom 1 will decrease, according to Michael, in the following order; 2-3-5-6-4-(9-10-11)-8. This scale was derived after a study of a great number of reactions which had previously been investigated.

As was shown in the aforementioned study of the monobrom



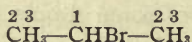
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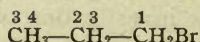
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derivatives of isobutane, bromine has a greater tendency to combine with the tertiary than with the primary carbon atom. This can be explained by the fact that the tertiary carbon atom (I) has nine hydrogen atoms in position 3, while six of these are in position 4 with respect to the primary carbon atom (II).

In the case of the propyl bromides Michael had concluded<sup>4</sup>



III



IV

that isopropyl bromide (III) would be the more stable because it has six hydrogen atoms in position 3, while in the normal bromide (IV) three of these have been moved to position 4. This conclusion he believed was confirmed by the results of addition of halogen hydrides to alkenes.

As was to be expected, and as will be shown below, catalytic influences determine the result in such cases. Conclusions regarding stability can only be drawn when the compounds concerned can be obtained in a state of equilibrium, as has now been done.

<sup>4</sup> *J. für prakt. Chem.* **60**, 447 (1899); *J. Amer. Chem. Soc.*, **32**, 1004 (1910).

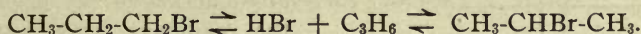


## I. Rearrangement of the Propyl Bromides, and Equilibrium in the Gaseous State

Aronstein<sup>5</sup> showed that at 280° C. normal propyl bromide undergoes rearrangement to isopropyl bromide. He believed that if he could heat the normal bromide for a sufficiently long time and to a sufficiently high temperature, the process of isomerisation would eventually go to completion giving pure isopropyl bromide. However, he later found that the reaction did not go to completion even after heating for one hundred hours.<sup>6</sup> In order to explain this, he attempted to show that isopropyl bromide changed, partially at least, to normal propyl bromide; but obtained only doubtful evidence. Faworsky,<sup>7</sup> however, succeeded by prolonged heating in sealed tubes at 250° C. and repeated removal of the portion isomerised, in converting about 20% of iso- into normal propyl bromide and showed, therefore, that this is a reversible reaction. However, there is nothing in his results to show the position of equilibrium.

Michael and Leupold<sup>8</sup> found that isomerisation was noticeable at 184° C. They heated the liquid bromides in tubes to 237° and 262° C. for one hour, getting 17 to 20% isopropyl bromide from the normal isomer, but they found that the rearrangement of iso- to normal propyl bromide took place to only an immeasurably small extent. Because of signs of decomposition these experiments were not continued to an equilibrium point.

It can now be stated with certainty, as shown below, that when either iso- or normal propyl bromide is heated to a sufficiently high temperature we get dissociation and isomerisation with the following equilibria:



Faworsky (*loc. cit.*) believed this to be the course of the reaction, though Michael and Zeidler<sup>9</sup> believed that the bromides could change directly without going through the stage of

<sup>5</sup> *Ber.*, **14**, 607 (1881).

<sup>6</sup> *Rec. trav. chem.*, **1**, 134 (1882).

<sup>7</sup> *Ann.*, **354**, 325 (1907).

<sup>8</sup> *Ibid.*, **379**, 263 (1911).

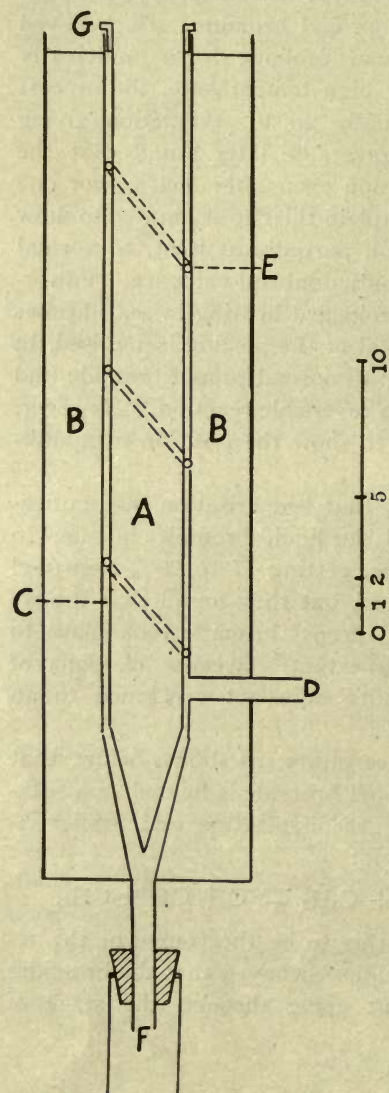
<sup>9</sup> *Ann.*, **393**, 92 (1912).

dissociation. The equilibrium desired is the ratio of the two undissociated bromides.

In the present investigation this ratio is obtained by heating

the bromides until equilibrium has been reached, then cooling suddenly and analyzing the products. The bromides are thus condensed while the dissociation products escape. The experiments below on the union of hydrogen bromide and propylene show that this reaction takes place so slowly that there is no danger of reunion of the dissociation products during the cooling process.

The procedure followed was to heat about ten grams of the bromide in large glass tubes. These tubes were of heavy pyrex glass of 3.3 cm. external diameter and 55 to 75 cm. long, sealed at one end, with the other end sealed to a 0.5 mm. capillary tube. They were thus sufficiently large so that on heating, all of the bromide would be converted into vapor. After the introduction of the bromide the capillary was further drawn down to a tip two to three inches long, of extremely fine bore. With the tube in a vertical position, the bromide was then slowly boiled so as to expel all the



air from the tube. The upper surface of the bromide vapor could easily be followed by the even ring of condensation



which gradually crept up the tube. When all of the air had been removed the end of the fine capillary was sealed.

These tubes were heated in furnaces for varying lengths of time; then the fine capillary was inserted into a specially constructed and particularly efficient brass condenser, Fig. 1, and the tip broken off. The inner and outer chambers, A and B, of the condenser were filled with ice and salt, so that the thin brass walls of the inner chamber, C, were well cooled. The gases entered at D and were given a spiral motion up through the condenser by the partition E. The condensed bromides dripped down at F, into a flask, while the hydrogen bromide and propylene escaped at a small opening in G. A test of the temperature of the gases at the outlet in G with an Anschutz thermometer showed it to be  $13^{\circ}\text{C}$ . Later this temperature was followed more accurately with a copper-constantan thermocouple and was found to range from  $8^{\circ}\text{C}$ . to  $15^{\circ}\text{C}$ .

The liquid products were usually freed of hydrogen bromide and dried by standing over anhydrous potassium carbonate; a few were washed with water and dried over potassium carbonate for a few minutes only. No appreciable difference was found in these results. Furthermore, as evidence that there was no reaction between potassium carbonate and the bromides, specimens of the pure bromides were left standing with the carbonate for 48 hours. The carbonate was washed with ether, dissolved in water and dilute nitric acid, and tested with silver nitrate solution. This gave no greater turbidity than a blank test with the original potassium carbonate. Also, repetition of the analysis of some of the mixtures after standing several months with potassium carbonate showed no alteration.

### Methods Employed in Testing the Mixed Bromides

1. Before applying any quantitative tests, a qualitative test for the presence of a normal bromide was performed with the first few experiments of each type explained in this paper. The nitrolic acid or pseudonitrole was formed from the normal or isopropyl bromides respectively and these were tested according to Richard.<sup>10</sup> The former gives a yellowish red color in alkaline solution, while the latter gives a blue color in acid so-

<sup>10</sup> *Ann. de Chem. et de Phys.*, [8] 21, 341 (1910).

lution. The primary nitro compounds also give copious white precipitates with lead acetate.<sup>11</sup>

2. The refractivities of the two bromides were tested at 25° C. with a Pulfrich refractometer and it was found that the refractivities of mixtures of the two isomers, plotted against the percentage composition, fell on a straight line. Before testing any of the mixed bromides by this method they were always completely distilled in a small apparatus which was so constructed that it was relied upon for retaining all of the bromides, while it was hoped that the distillation would free them of any dissolved propylene or hydrogen bromide, and possibly other impurities. It was soon found that very small amounts of unknown impurities were likely to shift the refractivity so that these results could not be relied upon for an accuracy greater than 10 to 15%, as shown by experiments 31 and 32. The data given for refractivity are thus to be taken with this reservation; but there are few cases in which the refractivity alone is depended upon.

3. The method of Michael and Leupold<sup>12</sup> was adopted as the most practicable for obtaining quantitative results. The mixed bromides are shaken in sealed tubes with an aqueous tenth normal solution of silver nitrate for three hours and the unused silver nitrate titrated by Volhard's method. In this time all of the isopropyl bromide reacts with the silver nitrate, while only 2.7% of the normal bromide reacts to give silver bromide. A single blank test with each of the pure bromides was in perfect agreement with the results of Michael and Leupold.

4. The products were shown to consist practically entirely of propyl bromide, by analysis for bromine by the Carius method. Some of the results are low by about 2% but this can be ascribed partly to the difficulty in getting the last traces of silver bromide out of the long tubes.

5. When a sufficient amount of the mixed bromides was at hand it was submitted to a fractional distillation in a still of small capacity, constructed similarly to those of Dufton.<sup>13</sup> The fractionating column of 50 cm. in length consisted of a

<sup>11</sup> V. Meyer *Ann.*, **171**, 42 (1874); *Ber.*, **8**, 1073 (1875); *Ber.*, **9**, 384 (1876).

<sup>12</sup> *Ann.*, **379**, 288 (1911).

<sup>13</sup> *J. Soc. Chem. Ind.*, **38**, 45 (1919).



spiral of number 18 gage constantan wire wound tightly around a fine glass rod of 0.3 cm. diameter. This in turn fitted tightly into a glass tube in such a way that the condensed liquid followed the spiral wire in returning to the flask, while the ascending vapors had to follow the spiral space between the wires. The insulation consisted of two air jackets made by surrounding the column with increasingly larger pieces of glass tubing.

Isopropyl bromide boils at 59–60° C. and the normal bromide at 71.5° C. With liquids boiling at these temperatures the total residue remaining in the still after everything possible had been distilled over, usually amounted to about 1.3 grams. The still was tested with a mixture of methyl and ethyl alcohols and was found to give a very satisfactory separation.

It was believed that it would take considerable time for the gaseous equilibrium to become established and it was known that reactions of this type are frequently very susceptible to the presence of catalysts. During the first experiments an attempt was therefore made to find some substance which would have the desired catalytic effect. The presence of foreign materials, however, appeared to induce decomposition of the bromides. In Table I a few results with catalysts are given. They show extensive change of iso- to normal propyl bromide, but no agreement, because of decomposition. The more conclusive experiments, summarized in Tables II and III, were all performed in pyrex glass tubes (which had been thoroughly cleaned before each experiment with hot bichromate mixture), without catalysts. In these experiments the tubes showed at most only a slight coating of decomposition products and the liquid products were colorless or but slightly yellow; this color always disappearing entirely upon the addition of potassium carbonate.

The mixed bromides were analyzed by the method of Michael and Leupold. The percents of isopropyl bromide, as given in the following tables, are in every case the averages of duplicate determinations which usually agreed within 1%. The time required for the escape of the gases into the condenser is given to show that the percentage composition of the bromides was independent of this time, that is, the condensation of the bromides was practically complete.

**Table I**  
**Experiments at 285–295° C with Catalysts**  
 (Starting with *i*-propyl Bromide)

No. of Exp.	Catalyst present	Time of heating	Time for gases to escape	% <i>i</i> -propyl bromide
1	HgBr <sub>2</sub>	4 days	1'20"	46.8
2	HgBr <sub>2</sub>	3 days	0'57"	48.3
3	Charcoal	11 hrs.	2'0"	58.8
4	BaBr <sub>2</sub>	27.5 hrs.	0'53"	Fractionated

The bromides from Experiment 4 were fractionated through the small spiral still. Although with the small amount of liquid the fractionation was necessarily imperfect, the presence of the normal bromide is confirmed.

Fraction I	59.8° to 61.0°	2.2 grams
Fraction II	61.0° to 64.2°	0.4 grams
Fraction III	64.2° to 70.3°	0.7 grams

The residue of about 1.3 grams was probably mostly normal propyl bromide.

**Table II**  
**Experiments at 285–295°C Without Catalysts.**  
 (Starting with *i*-propyl Bromide)

No. of Exp.	Time of heating	Time for gases to escape	% <i>i</i> -propyl bromide	% C <sub>3</sub> H <sub>7</sub> Br
5	23.5 hrs.	5'0"	67.9	
6	50 hrs.	2'9"	58.6	100.8
7	71 hrs.	3'30"	54.7	
8	73.5 hrs.	3'55"	53.3	

**Table III**  
**Experiments at 285–295°C Without Catalysts**  
 (Starting with *n*-propyl Bromide)

No. of Exp.	Time of Heating	Time for gases to escape	% <i>i</i> -propyl bromide	% C <sub>3</sub> H <sub>7</sub> Br
9	11½ hrs.	15' 0"	47.6	
10	28 hrs.	1' 20"	48.1	
11	49 hrs.	1' 41"	52.2	
12	70 hrs.	4' 45"	54.3	97.9
13	70 hrs.	3' 0"	54.7	98.1
14	71 hrs.	7' 30"	54.7	97.8



These experiments show that a true equilibrium point has been reached, starting with either normal or isopropyl bromide. This equilibrium is attained after about seventy hours heating at 285–295°C. Equilibrium in the gaseous phase at this temperature exists when we have approximately 54.5% of isopropyl bromide, that is, a relatively small preponderance of iso- over normal propyl bromide.

Although the variation of the equilibrium point with temperature should be slight, in consequence of the very small difference in the heats of formation of such isomers, nevertheless an attempt was made to determine the ratio between the two bromides at equilibrium at a lower temperature. A few of these results are given in Table IV.

**Table IV**  
**Experiments at 200°C Without Catalysts**

No. of Exp.	Bromide used	Time of Heating	Time for gases to escape	%- <i>i</i> -propyl bromide
15	<i>i</i> -propyl	10 days	2' 45"	74.6
16	<i>i</i> -propyl	26 days	4' 30"	71.4
17	<i>n</i> -propyl	26 days	5' 30"	15.0

It was quite apparent that the equilibrium position had not been nearly reached from either end and no further experiments were performed at this temperature.

## II. The Union of Hydrogen Bromide With Propylene

Michael believed that it should be possible to draw conclusions regarding the energy relationships of two isomeric alkyl halides from data showing the proportions in which these two isomers were formed by the union of the hydrogen halide with the unsaturated hydrocarbon. However, in the case of hydrogen bromide and isobutene, it was found<sup>14</sup> that the ratio of the velocities of formation of iso- and tertiary butyl bromide was subject to great variations and that this reaction was greatly influenced by catalytic action.

The first attempt to predict which of two isomers would be formed by such a reaction was the empirical rule of Markownikoff<sup>15</sup>: "When an unsymmetrical hydrocarbon combines with a

<sup>14</sup> *J. Amer. Chem. Soc.*, **39**, 1990 (1917).

<sup>15</sup> *Ann.*, **153**, 256 (1870).

halogen hydride, the addition will take place in such a way that the halogen is joined to the least hydrogenated carbon atom; that is, to that carbon atom which is most under the influence of other carbon atoms". Markownikoff then continues and cites among other examples of this rule the addition of hydrogen iodide to propylene as giving only isopropyl iodide. This reaction was first carried out by Bertholet<sup>16</sup> and was further studied by Erlenmeyer,<sup>17</sup> Butlerow<sup>18</sup> and Michael.<sup>19</sup> The latter three investigators found, besides the isopropyl iodide, a very small proportion of the normal iodide. Michael believed<sup>20</sup> that in the propyl bromides formed by a similar reaction, the proportion of normal to iso-propyl bromide would be even smaller than that found for the iodides. However, this has not been found to be the case.

In the following experiments it will be shown that the union of hydrogen bromide and propylene is also subject to a wide variation which is probably due to catalytic action, the exact cause of which has not been ascertained. However, sufficient results have been obtained to indicate that the relative velocities of formation bear no relation to the relative stabilities of the two bromides as determined in Part I above.

### Reaction in the Gaseous State

#### (a) EQUIMOLECULAR QUANTITIES OF PROPYLENE AND HYDROGEN BROMIDE IN LARGE BULBS.

The procedure followed consisted in allowing the reaction to take place in a large bulb or flask. The bulb was evacuated and heated to the temperature of the experiment. Equal molecular quantities of the two gases, that is, one half atmosphere of each—as measured by a manometer connected to a pressure adjusting device—were introduced at the beginning of each experiment. The pressure in the bulb was rather carefully followed during the course of the reaction by means of this manometer. In some cases further amounts of the gases were added after the pressure had considerably decreased. In

<sup>16</sup> *C. R.*, **54**, 1350.

<sup>17</sup> *Ann.*, **139**, 228 (1866).

<sup>18</sup> *Ann.*, **145**, 275 (1868).

<sup>19</sup> *J. für. prakt. Chem.*, **60**, 445 (1899).

<sup>20</sup> *J. für. prakt. chem.* **60**, 447 (1899); *J. Am. Chem. Soc.*, **32**, 1004 (1910).



order to minimize the possibility of the admission of air into the reaction vessel the following procedure was followed. All connecting tubes were first evacuated. The propylene was liquefied (b. pt.  $-50.2^{\circ}\text{C}.$ ) in a small bulb surrounded by carbon dioxide snow and ether. This bulb was then attached to the evacuated connecting tubes, placed in an ice and salt freezing mixture and permitted to boil, the gaseous propylene passing over calcium chloride. A stopcock giving an outlet to the air was opened and the propylene was boiled until there was a steady flow at the outlet and it was thought that any residual air had been swept out of the tubes. This stopcock was then closed and one leading to the bulb opened. Propylene was boiled into the bulb until the pressure measured one half atmosphere. An almost colorless solution of hydrogen bromide in water, saturated at the temperature of an ice and salt freezing mixture, was connected by another inlet and very gently warmed. The solution gave off hydrogen bromide which was dried by passing over calcium bromide and phosphorus pentoxide. When dense fumes appeared at the open outlet, this was closed and the hydrogen bromide passed into the bulb until the total pressure was one atmosphere.

The reaction was at first allowed to go on at a temperature which was sufficiently high to keep the bromides formed in a gaseous state. However, it was soon found that the union took place but slowly at these temperatures ( $80$  to  $130^{\circ}\text{C}.$ ) and some experiments were tried at temperatures as low as about  $21^{\circ}\text{C}.$

Liquid naturally collected in the bulbs at these lower temperatures and it was thought that the presence of a liquid surface might exert a catalytic effect leading only to the formation of one of the two possible isomers. This had been found to be the case with the iso- and tertiary butyl bromides. However, in no instance was it found possible to assign any definite catalytic effect to the presence of liquid bromide, though the cause of the extremely wide variation in the composition of the products must undoubtedly be sought in catalytic action.

But little liquid product could be obtained from the 3.3 liter bulb which was first used and only one of these experiments yielded sufficient product to test. The 12 liter bulbs which were used in a large majority of the experiments usually gave

from ten to fifteen grams of the mixed bromides. The products were, in general, clean, most of them being colorless and the rest but slightly yellow; this color disappearing upon treatment with potassium carbonate. Several of the products were found to have a sharp odor. It is believed that this odor appeared whenever slight traces of some unknown impurity, due probably to oxidation, were present, since it was noticeable in products which gave an analysis very close to 100% for  $C_3H_7Br$ . No trace of this odor was ever noticed in the products of any of the rearrangement experiments. However, it was found that when the tubes from these experiments, still containing the dissociated gases, were left open to the air, a product having this characteristic sharp odor was formed.

*Expt. 18.*—The 3.3 liter bulb was evacuated to 1.5 mm. pressure and heated to 100°C. One half atmosphere each of hydrogen bromide and propylene were introduced. The pressure decreased more regularly than in most of the later experiments until in three days it was 55.7 cm. The bulb was then removed from the furnace and rapidly cooled. By the refractivity test the product appeared to contain 76% *normal propyl bromide*.

The following experiments were all carried out in 12 liter pyrex bulbs, the necks of which were drawn down and sealed to capillary tubes with stopcocks.

*Expt. 19.*—The bulb was evacuated to 1 mm. pressure and filled as in Experiment 18 at 105°C. In three days the pressure had decreased to about 54 cm. and appeared to be remaining almost constant. An effort was therefore made to increase the reaction velocity by warming the bulb. The temperature was accordingly gradually raised to 130°C. Six days after starting the experiment and at a pressure of 60.8 cm. the bulb was removed from the furnace and quickly cooled. The liquid product was washed with dilute sodium hydroxide solution and finally with water and then dried over anhydrous potassium carbonate and sodium bromide. The liquid undoubtedly had the order of the normal bromide and gave the nitrolic acid test for the presence of a normal halide. A test by the refractivity method indicated the presence of 97% of *normal propyl bromide*.

The major portion of the product was then submitted to a



distillation in the small spiral still. It was found impossible to get any liquid over below  $66.0^{\circ}\text{C.}$  showing that the percentage of isopropyl bromide must have been very small indeed. Only two fractions were taken: I,  $66.0^{\circ}\text{C.}$  to  $70.0^{\circ}\text{C.}$  weighed 1.9 grams; while II,  $70.0^{\circ}\text{C.}$  to  $70.6^{\circ}\text{C.}$  weighed 3.6 grams. This latter fraction, plus the 1.3 grams of residue must be considered as practically pure normal propyl bromide, while the lower boiling fraction also contained a large proportion of the higher boiling isomer.

*Expt. 20.*—This experiment was carried out similarly to Experiment 19 except that the temperature was kept between  $133^{\circ}\text{C.}$  and  $200^{\circ}\text{C.}$  in an effort to decrease the time required. However, the pressure decreased very slowly and in fourteen days after a total decrease of only 13 cm. it was found that considerable decomposition had taken place and that the liquid had a sharp odor. The refractivity of the product was slightly beyond that of the pure normal bromide. It gave a nitrolic acid as shown by the reddish color of its alkaline salt, also a primary nitro compound as shown by the copious white precipitate with lead acetate.

*Expt. 21.*—In this experiment some mercuric bromide was sucked into the bulb before starting the experiment in the hope that this might definitely catalyze the reaction. The temperature of the experiment was  $94^{\circ}\text{C.}$  and the decrease in pressure 17.1 cm. Upon removing the bulb from the furnace it was noted that the presence of foreign material had produced the same results as in the rearrangement experiments—namely: it had induced a great deal of decomposition.

*Expt. 22.*—No catalyst was used in this experiment which in other respects was similar to the preceding ones. The temperature of the bulb during the reaction, which lasted for only one day, was  $125^{\circ}\text{C.}$  In this time the pressure had decreased 13.8 cm. Upon taking the bulb out of the furnace it was found to be perfectly clean in appearance and the liquid which collected was quite clear and colorless. The product was washed with dilute sodium hydroxide and water and then dried over fused potassium carbonate. The odor was that of the normal bromide with a slight trace of the sharp smelling impurity. The product gave a nitrolic acid as determined by its reddish yellow alkaline salt and a nitro compound as shown

by the copious white precipitate with lead acetate. The major portion of the product was put through the small spiral still with the following results:

Fraction I, 63.0°–66.0° consisted of 0.3 gram (contained sharp smelling impurity).

Fraction II, 66.0°–70.0° consisted of 0.5 gram.

Fraction III, 70.0°–71.0° consisted of 1.4 grams.

Residue . . . . . consisted of 1.3 grams.

*Expt. 23.*—This experiment was exactly similar to the previous one except that the reaction was allowed to take place at room temperature in a room which was usually at about 25° C. in the day time. After fourteen days during which time the total decrease in pressure was 56.5 cm., it was found that the bulb had remained perfectly clean with no trace of decomposition. The liquid was purified by standing over anhydrous potassium carbonate. Analyses were made by the method of Michael and Leupold, (*loc. cit.*) and showed the presence of 55.8% *normal propyl bromide*. A total analysis by the Carius method was carried out and gave a somewhat low result due to the overturning of the crucible containing the precipitate to be weighed. It was known that a small amount of silver bromide was lost, but the result gave 97.61% of  $C_3H_7Br$ . The product must have been practically pure  $C_3H_7Br$ .

*Expt. 24.*—In this experiment the mixed gases were kept at 42° C. for one month while a total decrease in pressure of 61.8 cm. was noted. Upon cooling, the bulb was found to be absolutely clean and there was no trace of sharp odor to the product. It was left standing over anhydrous potassium carbonate. This was analyzed as in Experiment 23 and gave results indicating the presence of 99.9% *normal bromide*. A total analysis gave 99.29% of  $C_3H_7Br$ . The liquid was put through the small spiral still but as it was run through rather too rapidly and a thermometer with a comparatively large bulb was used the results were not very good. However, over 80% came over at the boiling point of normal propyl bromide.

*Expt. 25.*—The temperature of this experiment was 42° C. After seven days during which a decrease in pressure of 24.7 cm. had taken place, the bulb was removed from the furnace. No decomposition or charring had taken place but the sharp odor



was noticeable in the liquid product. Analysis gave 73.1% *normal propyl bromide* and 99.56%  $\text{C}_3\text{H}_7\text{Br}$ .

*Expt. 26.*—In this experiment one half atmosphere each of propylene and hydrogen bromide were put into the bulb at room temperature. The bulb was then raised to  $80^\circ\text{C}$ . and kept at this temperature for six days. When it was taken out of the furnace and cooled, only a very small amount of liquid collected—too small to remove for analysis. The bulb was opened to the air and allowed to stand. Four days later it was found that considerable liquid had formed. This was undoubtedly due to the catalytic effect, probably of the liquid layer, possibly of something which had entered with the air. The liquid when purified with fused potassium carbonate had the same sharp odor. This could not have been due to unsaturated products as a test with a dilute bromine solution showed no sign of the existence of a double bond. Analysis gave 75.42% *normal propyl bromide*.

Distillation of 15.6 grams of this product through the small spiral still, the temperature being followed by means of a copper-constantan thermo-couple, gave the following results:

Fraction I	$59.5^\circ$ to $61.8^\circ$	1.6 grams ( <i>i</i> -propyl bromide)
Fraction II	$61.8^\circ$ to $68.0^\circ$	2.7 grams
Fraction III	$68.0^\circ$ to $70.7^\circ$	3.4 grams
Fraction IV	$70.7^\circ$ to $71.5^\circ$	4.45 grams ( <i>n</i> -propyl bromide)
Residue		1.3 grams
Total		13.45

#### (b) IN TUBES AT ATMOSPHERIC PRESSURE UNDER VARYING CONDITIONS.

In these experiments the apparatus employed by Brunel<sup>21</sup> was used. The gases entered separately coming to temperature, mixing, and passing on through the tubes together. They were then cooled by passing through a spiral condenser surrounded by an ice and salt freezing mixture. This experiment was tried at various temperatures and with gases of varying degrees of moisture and purity. The tube of the spiral condenser was moistened with each, in turn, of the propyl bromides. However, under none of the conditions tried did the union take place to such an extent that anything could be collected.

<sup>21</sup> *J. Amer. Chem. Soc.*, 39, 1997 (1917).

## REACTION OF PROPYLENE AND AQUEOUS HYDROGEN BROMIDE

### (a) GASEOUS PROPYLENE AT ATMOSPHERIC PRESSURE.

Many attempts were made to absorb propylene by aqueous solutions of hydrogen bromide under atmospheric pressure. The original idea had been to investigate whether or not the liquid surface would so catalyze the reaction as to cause the formation of one—and one only—of the two isomeric propyl bromides. Simple as this reaction would at first glance appear to be, it was found to be accompanied by unexpected difficulties—probably due to unknown catalytic (“anti-catalytic”) effects. Most of the attempts were made by placing aqueous solutions of hydrogen bromide in a flask which was connected to a source of propylene (the propylene being under but slightly more than atmospheric pressure). The air was driven out of the flask, and the flask was placed on a shaker so as to present continually a fresh surface to the propylene. Ground glass surfaces were also tried in attempts to increase the absorbing area and thus the speed of formation of the addition products. It was necessary to avoid hydrogen bromide solutions of concentrations with too great a vapor pressure of hydrogen bromide, as in these cases the gaseous hydrogen bromide drove the propylene back out of the flask. At the same time, if the solution was too dilute no absorption took place. Frequently the solution would absorb several hundred cubic centimeters of propylene quite rapidly, and then—for no reason which could be determined unless it were due to dilution of the solution—would stop. Displacement of air which might have accumulated in the absorption flask did no good.

*Expt. 27.*—This was the only one of these experiments which yielded sufficient product to test. This product, after washing, and drying over fused potassium carbonate contained, as found by the refractivity test, 9% of *normal propyl bromide*.

Small amounts of mercuric bromide and aluminium chloride were added to solutions of hydrogen bromide in the hope that they might have a favorable catalytic effect—but without success.

Attempts to absorb propylene were also made by bubbling



the gas slowly through hydrogen bromide solutions, and by letting the gas pass slowly up through a long column filled with pebbles, down through which a solution of hydrogen bromide was slowly dripping. If absorption took place in this case it was only to so small an extent that any liquid bromide formed remained on the pebbles and did not drain down into the receiving flask.

An attempt was also made to follow the method used for the absorption of acetylene in sulfuric acid, using mercuric oxide as catalyst, as given by Ullman.<sup>22</sup> The effort was made in order to find which of the propyl alcohols would be formed by this reaction; but no absorption of the propylene occurred.

#### (b) LIQUID PROPYLENE IN SEALED TUBES.

In these experiments propylene was dried by passing through calcium chloride tubes and was liquefied by carbon dioxide snow. When hydrogen bromide was to be liquefied the drying agents used were calcium bromide and phosphorus pentoxide. The hydrogen bromide solutions used were always absolutely colorless, and appeared to give perfectly pure propyl bromides.

*Expt. 28.*—Liquid propylene and constant boiling aqueous hydrogen bromide were sealed in a tube at the temperature of carbon dioxide snow. The propylene was sufficient to react with approximately one half of the hydrogen bromide. This warmed to room temperature in the course of twelve hours and was then heated to 36° C. to complete the reaction. On opening there was but slight pressure in the tube. After purification the refractivity test showed 18% of *normal propyl bromide*.

*Expt. 29.*—A solution of hydrogen bromide saturated at the temperature of an ice and salt freezing mixture was sealed up with enough propylene to react with about three quarters of the hydrogen bromide in the solution. This was finally warmed in water at 50° C. From the pressure observed when the tube was opened this appeared to contain unused propylene. Refractivity indicated the presence of only 3% *normal propyl bromide*—and this may mean none at all.

*Expt. 30.*—This tube contained liquid hydrogen bromide and an excess of liquid propylene when sealed. On opening the

<sup>22</sup> *Enzyklopädie der technischen chemie*, 1, 94 (1914).

excess propylene boiled off. The refractivity of this sample was slightly beyond that of pure isopropyl bromide. The boiling point was 57° C. In the presence of excess propylene only isopropyl bromide had been formed and none of the primary isomer.

*Expts. 31 and 32.*—These experiments are duplicates in every respect except that in 31 the proportion of propylene to hydrogen bromide at the start of the experiment was considerably greater than in 32. Hydrogen bromide solution saturated at 0° C. and liquid propylene were sealed in these tubes. The products were washed with water and dried over fused potassium carbonate. The results of these experiments were as follows:

No. of Expt.	Analysis with n/10 AgNO <sub>3</sub>	Analysis by refractivity	% C <sub>3</sub> H <sub>7</sub> Br
31	28.5% <i>n</i> -propyl bromide	12% <i>n</i> -propyl bromide	97.97
32	35.5% <i>n</i> -propyl bromide	25% <i>n</i> -propyl bromide	100.7

Most of the product from 31 was distilled. The greater part of this was found to be pure isopropyl bromide, but a small amount came over at the boiling point of the normal bromide. The distillation was run through too quickly for quantitative results.

A part of the product from 32 was also distilled. The results were as follows:

Fraction I	58.5° to 60.0°	weighed 7.3 grams
Fraction II	60.0° to 61.0°	weighed 8.9 grams
Fraction III	61.0° to 66.5°	weighed 2.1 grams
Fraction IV	66.5° to 71.0°	weighed 1.2 grams
Residue		weighed 1.3 grams

*Expt. 33.*—An attempt was made to use hydrogen bromide solution of half the strength of those used in 31 and 32 but after standing for several days the tube exploded.

These results appear to indicate that if the formation of one or the other isomer is not entirely dependent upon catalytic effects which have not been determined as yet, it may depend upon the relative amounts of the reacting substances. In Experiments 31 and 32 the greater ratio of hydrogen bromide to propylene in 32 was accompanied by formation of more normal propyl bromide. In Experiments 28 and 29 the relative values (18:3) of the normal bromide, although determined only



by refractivity, must indicate something; and in this case again more of the normal propyl bromide has been formed in that case where the ratio of hydrogen bromide to propylene is greater. In Experiment 30 a large excess of propylene is seen to result in the formation of only isopropyl bromide.

These results when compared with the equilibrium between the bromides, as found in Part I, confirm the previous statement that there is no relation between the relative stability of the compounds in question and this relative rates of formation from hydrogen bromide and propylene.

### III. Dissociation of the Propyl Bromides

The measurement of the dissociation of the propyl bromides was undertaken by the method used for the butyl bromides.<sup>23</sup> Contrary to Konowaloff,<sup>24</sup> and Michael and Zeidler (*loc. cit.*) there was no difficulty in obtaining dissociation, although very little was observed at the temperatures at which they worked. As the addition of hydrogen bromide to propylene was found to go more slowly than with isobutene, so the dissociation of the propyl bromides always required at least several days as compared with the few hours required for the butyl bromides to reach a state of equilibrium. Owing to the long heating required the decomposition was frequently so great that good results could not be obtained, and thus the dissociation constants are only approximate. They are, however, surprisingly close to those found for the butyl bromides. Catalysts, when tried, were found to induce decomposition, rather than to aid the dissociation.

In the following tables the calculated pressure (P calc.) is that pressure which the amount of bromide used in a given experiment would exert at the temperature of the experiment, provided that there were no dissociation. In the last column the per cent dissociated is indicated by the excess of the values over 100. The dissociation constant is represented by K.

*Expt. 34.*—No catalyst was present in the bulb during this experiment.

2.701 grams of isopropyl bromide were used in a vapor density bulb of 1131 c.c. capacity at 25° C.

<sup>23</sup> *J. Amer. Chem. Soc.*, **39**, 1978 (1917).

<sup>24</sup> *Ber.*, **18**, 2808 (1885).

Time	Temp.	P obs.	P calc.	$100 \frac{P \text{ obs.}}{P \text{ calc.}}$
1 hr.	124°	47.66	48.07	99.15
5 hrs.	152°	51.52	51.46	100.1
11 hrs.	191°	58.36	56.18	103.9
16 hrs.	229°	63.31	60.78	104.2
21 hrs.	237°	68.5	61.75	110.2
39 hrs.	296°	111.20	68.88	161.4
45 hrs.	296°	118.38	68.88	171.9
58 hrs.	301°	118.01	69.50	169.8
65 hrs.	121°	48.15	47.71	100.9

At 296° C.: per cent dissoc. = 71.9;  $K = 0.03572$ .

It is to be noted that after only seven hours, at a lower temperature at the end of the experiment, the dissociation products had almost completely recombined.

*Expt. 35.*—In this experiment mercuric bromide was present in the vapor density bulb as a catalyst. In every case the pressure given as the observed pressure is the observed total pressure in the bulb minus the calculated pressure of the mercuric bromide; that is, it is the observed pressure of the propyl bromides and their dissociation products.

2.379 grams of isopropyl bromide were used in a vapor density bulb of 1218.550 c.c. capacity at 25° C.

Time	Temp.	P obs.	P calc.	$100 \frac{P \text{ obs.}}{P \text{ calc.}}$
3 hrs.	134°	40.78	40.29	101.2
17 hrs.	312°	100.36	57.91	173.3
28 hrs.	301°	98.12	56.82	172.7
47 hrs.	299°	99.13	56.62	175.1
52 hrs.	129°	67.14	39.80	168.7
64 hrs.	126°	63.09	39.50	159.7

At 299° C.: per cent dissoc. = 75.1;  $K = 0.03874$ .

In this experiment, after seventeen hours at a temperature near 126° C. at the end of the experiment, very little recombination had occurred.

Due to the low molecular weight of the substance under investigation so little of the material could be used in the vapor density bulbs that it was impossible to get any liquid out of them at the completion of an experiment for analytical purposes.

In general the results of these experiments did not agree well and only the two most reliable ones have been given.



## PREPARATION OF MATERIALS

The hydrogen bromide used throughout this research was made catalytically by bubbling electrolytic hydrogen through bromine, kept at about 40°C., and passing the mixed gases through a quartz tube, partially filled with platinized asbestos and electrically heated to a red heat. With the exception of one rubber stopper at the entrance to the quartz tube, there were no rubber connections on the apparatus. Phosphoric acid was used as lubricant in the stopcocks and ground glass joints. The apparatus gave colorless solutions of hydrogen bromide.

Isopropyl alcohol, was prepared by the reduction of acetone under pressure, using nickel oxide as catalyst. The method is that of Ipatiew<sup>25</sup> as used by Brunel, Crenshaw, and Tobin.<sup>26</sup> The alcohol was then dried over lime and fractionated through tall Hempel columns.

Isopropyl bromide was made from hydrogen bromide and isopropyl alcohol, in the main according to Norris.<sup>27</sup> The alcohol was quickly poured into a saturated hydrogen bromide solution. A steady stream of hydrogen bromide was kept bubbling through the solution. The heat of the reaction, together with the stream of hydrogen bromide was sufficient to carry the greater portion of the bromide formed up through a Hempel column.

The reaction mixture was finally warmed, but it was not necessary at any time to boil it. The bromide was collected under water, washed with dilute sodium hydroxide and water, dried over calcium chloride and phosphorus pentoxide, and fractionated.

The normal propyl bromide used in this research had been made and fractionated previously but was refractionated before using.

The propylene was prepared according to the method of Freund<sup>28</sup> by dropping isopropyl iodide upon a mixture of alcoholic potassium hydroxide and powdered potassium hydroxide

<sup>25</sup> *C. A.*, **1**, 2878 (1907).

<sup>26</sup> *J. Amer. Chem. Soc.*, **43**, 561 (1921).

<sup>27</sup> *A. C. J.*, **38**, 637 (1907).

<sup>28</sup> *J.*, 400, (1882).

in a Michael retort.<sup>29</sup> To every part of iodide, one part by weight of a one to three alcoholic solution of potassium hydroxide and in addition to this one half part by weight of powdered potassium hydroxide were used. One half mole of the iodide gave a little over eleven liters of propylene at room temperature. The propylene was collected and kept over water in glass gasometers.

The isopropyl iodide used in the above preparation was made according to the directions of Adams, Kamm and Marvel.<sup>30</sup>

### Summary

The equilibrium between normal and isopropyl bromides and their dissociation products, hydrogen bromide and propylene, at 290° C., has been studied. The ratio determined was 54.7% of isopropyl bromide to 45.3% of normal propyl bromide.

It has been shown that catalytic influences come into play in the formation of these bromides from hydrogen bromide and propylene, so that reaction between the gases usually gives almost entirely normal propyl bromide, even in the presence of a liquid surface; while the reaction of liquid propylene with liquid or aqueous hydrogen bromide always gives at least a large proportion of isopropyl bromide.

A dissociation constant has been determined for the propyl bromides and this has been found to be of the same order of magnitude as that of the butyl bromides.

<sup>29</sup> *Ber.*, **34**, 4958 (1901).

<sup>30</sup> *Univ. of Ill. Bull.*, **XVI**, 21 (1919).



## VITA

I, Helen Goldstein Rafsky, was born in New York City in 1897. My parents are Albert Sigmund Goldstein and Charlotte Frank Goldstein. I attended the Training Department of Hunter (then Normal) College and the Hunter College High School until 1914, when I entered Barnard College. In 1918 I received a B.S. degree from Barnard College, Columbia University. From 1918 to 1919 I was Scholar in Chemistry at Bryn Mawr College; from 1919 to 1921, Fellow. From 1921 to 1922 I was Helen Schaeffer Huff Memorial Research Fellow.

My preliminary examinations for the Ph.D. degree were taken in November 1921. My major subject was Organic Chemistry under Dr. Roger Frederick Brunel; my associate minor was Physical Chemistry under Dr. James Llewellyn Crenshaw; and my independent minor, Physics, under Dr. James Barnes. I wish to express my sincere appreciation of the very able instruction I have received from these professors and of their continued interest in my work.

In conclusion, I wish to state that the investigation described in the preceding pages was undertaken at the suggestion of Professor Brunel and carried out under his direction. I feel that whatever merit the work may possess is due to his kindly interest and careful direction, and I desire to express my appreciation of his valuable instruction.







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